Osmium: An Appraisal of Environmental Exposure

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In the U.S., the chief source of new osmium is copper refining, where this metal is produced as a byproduct. Probably less than 10% of the osmium in the original copper ore is recovered, and 1000–3000 oz troy of osmium is lost each year to the environment as the toxic, volatile tetroxide from copper smelters. In 1971, about 2000 oz troy of osmium was domestically refined, most of which was from secondary sources. An additional 4169 oz troy of osmium was toll-refined. Major uses for osmium tetroxide identified are for catalysis, especially in steroid synthesis, and for tissue staining. Minor uses of osmium metal are for electrical contacts and for imparting hardness to alloys for mechanical pivots, etc. Unreclaimed osmium tetroxide that reaches wastewater streams is probably rapidly reduced by organic matter to nontoxic osmium dioxide or osmium metal, which would settle out in the sediment of the water course. Waste osmium metal, itself innocuous and chemically resistant, would be oxidized to the toxic tetroxide if incinerated.

Because of the small amounts used and their wide dispersal, the amounts of osmium tetroxide in wastewater and air should pose no hazard to man or the environment. The chief acute toxic effects of osmium tetroxide are well known and include eye and respiratory-tract damage. Few data are available that provide information on possible effects of nonacute exposure resulting from environmental contamination by osmium. However, workers continually exposed to osmium tetroxide vapors (refiners and histologists) and rheumatoid arthritis patients who have received intra-articular injections of osmic acid solutions have shown no apparent damage from exposure to low levels of osmium.

Introduction

Osmium is rare in nature, is quite expensive, and has achieved only limited commercial use. Existing markets for this metal are very competitive; consequently, suppliers and dealers are reluctant to disclose information on either uses or consumers. For these reasons, only scattered data are available on the consumption and ultimate disposition of osmium and its compounds.

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The following discussion summarizes available information on the natural occurrence, refining, processing, uses, and disposal of osmium and its compounds as well as the effect of these activities on man and the environment. The nature of distribution pathways and the extent of ecological damage by osmium have been based primarily on subjective evaluations.

Background

Osmium was discovered by Smithson Tennant in 1804 (1). This element was first isolated from the black powder remaining after

platinum had been recovered from platinum-bearing ores. Osmium occurs naturally in association with iridium and other platinum group metals. The most important source of this metal is as an alloy called osmiridium whose osmium content may vary considerably. The osmium content of osmiridium recovered as a by-product of gold mining in South Africa, for example, varies from 24.0 to 44.5% (2). The most common composition, however, contains about 35% osmium and 30% iridium. The rest of the alloy consists mainly of platinum, rhodium, and ruthenium. Osmiridium having the highest known osmium content was reported by Vernadsky (3) in 1914 to contain 80% osmium.

The principal sources of platinum metals in the world are the Bushveld Complex of South Africa; the Sudbury District of Ontario, Canada; and the Norilsk and the Kola Peninsula regions of the USSR (4). Minor sources are placer deposits in the Urals, Alaska, Colombia, Ethiopia, Japan, Australia, and Sierra Leone. Since 1934 Alaska has ranked fifth in the world production of platinum. The Witwatersrand District of the Bushveld Complex of South Africa, however, is the world's greatest producer of osmiridium, the principal source of osmium.

Platinum metals have been found in 22 states of the United States, but only Alaska is a major producer (5). The principal sources in Alaska are the Goodnews Bay District, Western Alaska, and a copper lode on Kasaan Peninsula, Southeastern Alaska, which was worked several years but is now closed. A small fraction (19%) of the domestic production of osmium came from the Goodnews Bay mining operation in 1970. In California and Oregon, small amounts of platinum metals including osmiridium are recovered as a by-product of gold placer mining. Several ounces of osmium are recovered as a by-product of the copper and gold ore processing industry. About 81% of the domestic production of osmium came from these latter two sources in 1970. Small gold−platinum and copper−platinum lodes have been mined in past years in the Rocky Mountain states, generally without a profit.

Mining and Processing

In 1970, about one-third of the free-world output of the platinum-group metals, which include osmium, was produced by International Nickel Company of Canada, Ltd. (INCO) (6) from nickel−copper lodes of the Sudbury District. Crude residues containing the platinum-group metals are produced from the Canadian ore and shipped to INCO's Acton Platinum Metals Refinery in London, England, where the platinum metals are separated and recovered in the pure form. Much of the osmium is returned to Canada, exported to the United States, and sold to Engelhard Industries of Newark, New Jersey. No figures on the total amount of osmium recovered each year from these mines have been found.

The Witwatersrand District of South Africa is the world's largest producer of osmiridium, the principal source of osmium. Rustenberg Platinum Mines, Ltd., produces platinum-group metals from this ore, which is mined chiefly for platinum, and contributes almost two-thirds of the free-world output of platinum-group metals. The bulk of the Rustenburg production goes to Johnson, Matthey and Company, Ltd., in Great Britain for processing. Much of this metal is eventually sold in the United States by subsidiary companies, Matthey Bishop, Inc., and Johnson, Matthey and Company, Inc.

Engelhard Industries also refines concentrates and platinum-bearing matte from the Brakesprite Mine in the Republic of South Africa and from Falconbridge Mines of the Sudbury District.

As previously mentioned, a small quantity of osmium is produced from the United States mining operations. The major fraction of the domestically produced osmium is recovered as a by-product of copper refining in Maryland, New Jersey, Texas, Utah, and Washington (F. C. Mitko, U.S. Bureau of Mines, personal communication, November 1972). Some osmium is also recovered from a placer platinum deposit at Goodnews Bay, Alaska, and refined by Matthey Bishop, Inc., in Malvern, Pennsylvania.

Mining and Refining of Osmium

The method of mining employed to recover osmium-containing ore is dependent on the ore body. Alluvial deposits are commonly recovered by dragline dredging. The alluvial deposits be-

ing mined include the Goodnews deposit in Alaska, gold placers in the Ural Mountains of the USSR, and the Colombian deposits. Ores from these deposits are generally concentrated by gravity separation. This same technique is used in South Africa to concentrate osmiridium.

Copper and nickel ores, which contain platinum metals, are commonly mined by open-pit methods. No attempt is made to separate the platinum metals from the major component of the ores. It is estimated that 1 oz of the platinum metals is recovered from 35 tons of copper produced in the U.S.; however, no serious effort is made to recover the precious metals in high yield.

The platinum-group metals in the Sudbury District of Canada are mixed with the sulfide ores of copper and nickel (7). Concentrates of the copper and nickel sulfides are obtained by magnetic and flotation techniques. INCO processes about 90% of the ore mined in the Sudbury District (5). In the INCO recovery and separation process, the copper−nickel concentrate is roasted and then blown to give a Bessemer matte. The bulk of the platinum metals is separated from the nickel and copper during slow cooling of the Bessemer matte and is removed magnetically. After smelting and magnetic separation, the enriched alloy, containing all six platinum-group metals, is electrolytically refined. The anode slimes produced during electrolysis contain the platinum metals. Smaller amounts of platinum metals are obtained from nickel refining by the Mond carbonyl process and from electrolytic refining of nickel concentrates. In conventional treatment for base metal removal, the anode slimes are often sulfated at 600°F to remove residual nickel and copper. After extracting with water to recover the copper and nickel, the concentrate that remains contains the precious metals. To recover the precious metals, the concentrate is calcined in air at 1500−1800°F to eliminate sulfur, selenium, and arsenic impurities. Unless precautions are taken to recover osmium, any osmium that survived the 500−600°F sulfating reaction (described above) would probably be lost in the calcining operation.

To retain the osmium during sulfation, the sulfation temperature is reduced to 400°F (8). Under this condition, less than 5% of the os-

mium is lost. To recover osmium, the calcining operation has been modified and provisions made to recover it during this operation. Gradually raising the temperature to 1500−1700°F during this calcining gives satisfactory osmium elimination for recovery in an alkaline solution. Our calculations indicate that about 20% of the osmium in the anode slimes is lost in the INCO process.

The majority of osmium is produced either as osmium tetroxide or metallic osmium. When the metallic form is to be produced, the tetroxide is precipitated as osmyltetraammine chloride $[OsO_2(NH_3)_4Cl_2]$ or as potassium osmate. The osmium metal is then formed by ignition of the former compound in hydrogen (7) or by treating potassium osmate with hydrochloric acid and hydrogen (8). If osmium tetroxide is the desired product, the precipitation and ignition steps are omitted, and osmium tetroxide is distilled directly from the process liquor.

Platinum-bearing nickel ore from the Republic of South Africa is crushed, ground, and gravity concentrated to give a "metallics" concentrate that contains 22% platinum metals and about two-thirds of the other precious metals. It is sent to Johnson Matthey Company, Ltd., at Brimsdown, England, for refining. The tailings from the gravity concentration are treated by flotation to give a concentrate that is smelted and blown to remove iron and to give a matte that contains about 48 oz/ton of platinum metals. The matte is sent to Johnson Matthey or treated near the mine by Matte Smelters, Ltd. The sulfide matte is smelted and separated by the tops-and-bottoms process to give ultimately blister copper and nickel sulfide with the bulk of the platinum metals. The nickel sulfide is treated much as the Sudbury nickel fraction, and the slimes from electrolysis of the nickel anodes are sent to England for refining (7).

At Brimsdown, the platinum metals are extracted by enriching the platinum containing materials to about 65% platinum metals and then treating the enriched product with acids to separate the individual platinum-group metals, followed by final refining.

The sources that account for the domestic U.S. production of osmium can be divided into five categories: new metal derived from crude platinum ores, osmium recovered as a by-

product of gold and copper mining, metal from the processing of crude platinum obtained from foreign sources, metal recovered from secondary sources such as scrap, and the osmium recovered from scrap and virgin materials from captive use by an industry (toll refined). The U.S. Bureau of Mines *Minerals Yearbook (9)* statistics on osmium produced from these sources are shown in Table 1. The amounts of new osmium derived from domestic and foreign sources are shown (New Metals).

Engelhard Industries, a major producer of osmium, estimates that approximately 2000 oz troy osmium was produced in 1971 in the U.S. (N. Carcillio, personal communication). This represents a significant increase over 1970 production if the figure is accurate. Over the 9-yr period from 1962 through 1970, approximately 934 lb was marketed in this country or about 100 lb (1460 oz troy)/yr.

The U.S. imported about 110,000 oz troy of unwrought or partly worked osmium, iridium, and osmiridium between 1968 and 1972 *(10)*. However, data are not available on how much of this is osmium, how much new osmium is recovered by refiners from this source, or how much is imported for refining and subsequent re-export. These voids in the data prevent making a mass balance of osmium produced (or lost in the process) and consumed in this country.

Available data on toll-refined osmium indicate that a large fraction of the osmium used in this country (50–70%) is controlled and used captively. The amount of osmium toll-refined each year is probably only a fraction of that held by individual industries.

Osmium Losses During Refining

The magnitude of losses of osmium during mining and refining is difficult to estimate. Where recovery of platinum group metals is an integral part of the refining operation, the percent recovery of all of the metals except osmium is believed to be quite high. Osmium, on the other hand, is easily lost during smelting or roasting of concentrated ores because of the ease of oxidation of the metal at elevated temperatures and the volatility of the oxidation product, OsO_4. International Nickel claims a recovery efficiency of 90% for precious metals, osmium excluded, from its Sudbury ore.

Platinum metals are recovered from gold and copper in refineries. It is difficult to estimate the quantity of platinum-group metals, particularly osmium, lost to the environment from

Table 1. Osmium produced in the U.S. [a]

Year	New metal, oz troy	Recovery from secondary sources, oz troy		Toll-refined, oz troy	Total U.S. production, oz troy	Sold to Industries in U.S., oz troy	Stockpile (refiners, importers and dealers), oz troy
1962	100		99 [b]		199	1125	2762
1963	189		273		462	1056	1531
1964	515		928		1443	1379	1936
1965	1199		763		1962	1634	1502
1966	1533		728		2261	1836	2559
1967	151		2377		2528	1823	2802
1968	95	672		2920	3687	1612	2402
1969	135	208		2197	2540	1472	2873
1970	149	121		958	1228	1707	1868
1971	—	352		4196	—	2126	—

[a] Data from *Minerals Yearbook (9)*.
[b] These sources were not reported separately until 1968.

these sources, since it is very dependent on the recovery process used. Between 1962 and 1970, 1714 oz troy osmium was recovered from these sources.

Data cannot be found on osmium and other platinum-group metals lost to the environment from ores not processed for these metals. It can generally be assumed, however, that the platinum-group metal content of these ores must be too low to justify the cost of the additional processing.

Recovery for Reprocessing

Various methods have been developed for recovering osmium from waste. The two major sources of osmium waste reprocessed in-house include catalysts (OsO_4) and fixative solutions (OsO_4) used in electron microscopy or for tissue staining. Scrap metal is simply returned to one of the refineries for reprocessing.

Osmium tetroxide used as a catalyst in steroid synthesis can be recovered from a steroid reaction mixture in reusable form and in 90–100% yield by treating the reaction mixture with thiourea under aqueous acidic conditions to form a thiourea complex of osmium, which is separated from the reaction mixture as an aqueous solution (11). The osmium–thiourea complex is then oxidized with hydrogen peroxide to osmium tetroxide, which is recovered in reusable form by standard methods; for example, by extraction with a water-immiscible organic solvent or by distillation. This process is reported to provide an effective method for removing osmium from the steroid reaction mixture, thereby preventing contamination of the steroid products with the highly toxic osmium tetroxide. Osmium tetroxide is reportedly a commonly used catalyst by many pharmaceutical houses for steroid production. The FDA and other government regulatory agencies do not analyze for such rare contaminants in pharmaceuticals, and it is not known whether osmium is a contaminant of steroids synthesized with osmium tetroxide as a catalyst.

Jacobs and Leggitt (12) reported recovering more than 80% of the osmium, as osmium tetroxide, from used fixative solutions. These fixative solutions commonly contain excess ferrous sulfate, which is added routinely to reduce the osmium tetroxide to osmium dioxide

to make it safe for disposal. Concentrated hydrocholoric acid and hydrogen peroxide are added to the tetroxide in water solution, and tetroxide is recovered by codistillation with water.

Schlatter et al (13) reported a similar method for regeneration of used osmium tetroxide fixative solutions, which also employed hydrogen peroxide to oxidize osmium to the tetroxide followed by codistillation of the newly formed tetroxide and water.

The Bureau of Mines estimated that 4169 oz troy of osmium was reclaimed by consumers for captive use in 1971 (F. C. Mitko, U.S. Bureau of Mines, personal communication, November 1972).

Markets for Osmium

Osmium has only limited use in relatively expensive end-products because of its high cost, fluctuating price, and short supply. The only commercial-product forms of osmium produced in any volume are osmium metal and osmium tetroxide.

In 1969 and 1970, the chemical industry purchased more than half of the osmium sold in the U.S. In 1971, this industry purchased almost three-fourths of all the osmium sold. Osmium consumed by chemical industry is apparently used for a variety of purposes, generally in small individual quantities. The medical industry is the next greatest user. These two industries consumed more than 95% of the total osmium production.

A survey of use, producers and distributors of osmium and osmium compounds yielded insufficient data to develop a mass balance for the osmium consumed annually in the U.S. Some large annual purchasers of osmium who account for about 25% of osmium sales were identified. In some instances, the uses made of these large purchases could not be determined. Table 2 contains a list of the largest sales of osmium identified annually.

The best assessment that can be made of osmium uses and consumption based on information obtained from producers, distributors, users, and a survey of the technical and patent literature and of trade journals is tabulated in the order of decreasing importance (Table 3).

Table 2. Largest osmium purchases.

Purchaser	Chemical Form	Use	Quantity purchased, oz
The Upjohn Company	OsO_4	Catalyst	130
G. D. Searle and Company	OsO_4	Catalyst	65
Unknown	Os metal	Electrical switches	200
Sandia Corporation	Os metal (?)	Unknown	10–50
Washington University	OsO_4	Tissue staining	12
U.S. Government [a]	OsO_4	Unknown	100–200

[a] The federal government purchases several large lots per year. This material is not purchased through GSA.

Table 3. Osmium uses and consumption.

Consumer	Uses	Quantity, %
Academic and industrial research laboratories	Chemical synthesis Analytical methods Catalysts Metallurgical Nuclear physics Biological	45
Medical laboratories	Tissue staining for electron microscopy Chemotherapy	35
Chemical manufacturer	Catalysts Steroids Polymers Hydrogenation	10
Electrical industry	Reed switches Light filaments Cathode tubes	5
Others	Mechanical pivots Bearings Phonograph needles Engraving tools	5

Research Uses

The major consumers of osmium appear to be academic and research laboratories. A survey of *Chemical Abstracts* indicates that over 150 new osmium compounds are synthesized and studied annually. Although no accurate estimate can be made of the amount of osmium used for this purpose, it appears to be significant. Many citations also appear on the research use of osmium as hydrogenation, oxidation, and hydroxylation catalysts. Although investigated extensively as a catalyst, osmium has apparently found only limited use for this purpose. The only known industrial use of osmium as a catalyst is the synthesis of steroids. The tetroxide is also used as a reagent for analyzing polystyrene–butadiene block polymers *(14)*.

Other literature citations that imply research-oriented uses of osmium include development of analytical methods, recovery of osmium from solutions, alloys of osmium, electroplating, use of osmium as nuclear targets, diffusion of osmium in metals, electron emission of osmium surfaces, spectral studies of osmium compounds, and many others. In addition, academic and other research laboratories consume osmium for histological staining of tissue and for electron microscopy studies. It must be concluded that a significant fraction of the 2000 oz of osmium sold to U.S. consumers annually is consumed in small quantities in a large number of laboratories for the above purposes.

A large fraction of the osmium used in the synthesis and characterization of new compounds is retained on laboratory shelves and may only be discarded after several years. The osmium used for other research purposes (catalysts, development of analytical methods, histological fixative and stain, etc.) is largely discarded down the drain after it is used.

It is not practical in most research laboratories to attempt to recover used osmium compounds because of the small quantities involved and the hazards associated with recovery. Recommended handling and disposal procedures are needed. As a minimum requirement, osmium(VIII) compounds should be reacted with a reducing agent, such as stannous chloride, to convert them to innocuous osmium dioxide or osmium metal prior to disposal.

Medical uses of Osmium

Considerable quantities of osmium tetroxide are used in medical research and in routine

clinical laboratory testing. The major use of this material is for histological examination of tissue specimens. Osmium tetroxide has long been recognized as an excellent fixative, applicable to a wide range of tissue types, which causes the least disturbance of cell structure (15). This property has resulted in the wide use of osmium tetroxide to prepare thin sections of tissue for electron microscopic examination.

Each of the osmium suppliers identified medical uses as major consumers of osmium compounds. The Medical School at Washington University, St. Louis, Missouri, for example, purchases about 16 oz of osmium tetroxide or 12 oz of osmium metal per year. Other major consumers identified include the Veterans Administration Hospital in Milwaukee, Rochester University, and Kent University. A limited survey of other medical schools and hospitals indicates that purchases of 1−15 oz of osmium tetroxide/yr are common for those institutions that have electron microscopes. The University of Kansas Medical School uses about 12 oz/yr, and the University of Missouri Medical School uses 1−2 oz/yr.

One supplier reported that several thousand grams of osmium tetroxide are purchased annually by the U.S. Government. This material is not purchased through GSA, which makes difficult the determination of quantities purchased and the uses. The seller of this osmium tetroxide is reported to have the best material for tissue staining; consequently, it is assumed that the majority of this material is used as a tissue fixative and stain.

Nearly all the osmium used for histological study is disposed of, without treatment, by flushing down the drain even by the larger consumers. Although recovery of osmium from used fixative solutions is relatively simple, it is not practiced widely because of the small amounts consumed annually in an individual laboratory and the hazards associated with recovery. Two similar methods, described in the literature for recovering this osmium, were discussed previously.

The only chemotherapeutic use of osmium identified is for treatment of arthritis (16). Osmic acid injections were found by von Reis and Swensson (17) to be an effective treatment for rheumatoid arthritis. They showed that the entire interior synovial layer coagulated as a result of the injections. Severe pain and a fever reaction were caused by the osmic acid injection. Other investigators have modified this treatment to combine osmic acid, a local anesthetic, and corticosteroids to reduce pain and other side reactions (18).

Chemical Industry

A substantial fraction of the osmium consumed by the chemical industry is apparently used for research purposes. Again, many of the research areas described previously are being investigated in chemical industry research laboratories.

The biggest single use of osmium is as a catalyst for steroid production. The chemical form of osmium used for this purpose is osmium tetroxide. It is used as a catalyst in the manufacture of such steroids as cortisone, hydrocortisone, prednisone, prednisolone, 2-α-methylprednisolone, 16-methylhydrocortisone, 6-α-fluoroprednisolone, acylates, and other derivatives of these compounds. A large fraction of the osmium used for this purpose is reclaimed and used again. The Upjohn Company purchases approximately 4000 g (130 oz troy) to replenish its stock annually (A. W. Schneider, Fine Chemical Division of the Upjohn Company, personal communication, November 1972). Merck at one time also used osmium tetroxide as a steroid dehydrogenation catalyst. This company now uses a new synthesis route which does not employ osmium. Three other large pharmaceutical houses contacted said that they did not use osmium as a catalyst.

Electrical Industry

No large uses of osmium by the electrical industry have been identified. It was estimated by one of the major osmium suppliers that 200 oz of osmium has been used in the production of reed switches (L. Greenspan, Engelhard Industries, personal communications). The use of osmium for this purpose is still experimental and only began to develop after a process was found for electroplating osmium. Should this use grow, it is anticipated that osmium used for this purpose

will be recycled with no substantial discard to the environment.

An osmium–tungsten alloy has been used for filaments for incandescent lamps. These filaments contain 3–30 wt-% osmium. These filaments are stable up to 2200°C and are used for high-intensity lamps such as the more expensive motion picture projectors.

Other Uses

Osmium has, over a number of years, been used for a variety of purposes. Most of these uses took advantage of the corrosion resistance and the hardness of the metal and its alloys.

Two alloys (20) of osmium (Os-86%, Ir-5%, Pt-10%, and B-1%; and Os-85%, Rh-5% and Pt-10%) were used as fountain pen nibs on the better pens until 1969, at which time pen manufacturers turned to a ruthenium–platinum alloy because of the fluctuating price and scarcity of osmium (J. Hauck, W. A. Sheaffer Pen Company, personal communication, February 1973). Osmium was also used for fingerprint detection; however, this use was discontinued because it caused dermatitis.

Osmium, or its alloys, is still used for pivots, bearings, phonograph needles, and engraving tools because of its hardness. The actual quantity used for this purpose could not be determined; however, it is small. It was noted by one manufacturer that 50,000 pivots could be fabricated from 1 oz of osmium.

Osmium is one component of a complex catalyst employed in a hydrogen-chlorine fuel cell patented by Union Carbide (21). Applications have been made for U.S. patents on modifications of electrodes for use in a fuel system of this type. No commercial fuel-cell system has been identified that employs this catalyst.

Environmental Effects

Osmium, being extremely rare, is not considered by the authors to be a serious environmental contaminant even though the toxicity of osmium tetroxide has been recognized almost from the time of the discovery of osmium. Following is a review of the sources of possible environmental contamination of os-mium and an estimate of their hazards.

Since osmium is found in nature primarily as the osmium–iridium alloy (osmiridium), there are no natural sources that should pose a hazard. Consequently, it must be concluded that any hazardous environmental contamination must be manmade.

The metal and its natural and synthetic alloys pose no recognized health hazard. The highly corrosion-resistant metal should survive intact for many years when disposed of as solid waste. However, osmium metal begins to oxidize in air at relatively low temperatures (approximately 100°C) to form osmium tetroxide. The temperature required for such oxidation is well above any ambient temperature that the element or its alloys might encounter in nature. Incineration of metal or alloys would convert it to the toxic osmium tetroxide; however, the quantities present in each unit of solid waste are too small to be of concern.

Since we have found no analytical information on osmium contamination of the biosphere even in the vicinity of likely man-made sources, we can only estimate the sources and magnitude of man-made contamination and its influence on the biosphere.

The U.S. reserves of osmium are almost entirely in copper ores. The largest sources of osmium lost to the air would come from roasting and smelting of copper concentrates, which contain small quantities of platinum-group metals. In a roasting and smelting operation, osmium present in the ore could be converted to the volatile osmium tetroxide. Osmium tetroxide begins to sublime below 30°C and boils at 130°C; consequently, typical stack gas temperatures are sufficiently high to maintain osmium tetroxide in the vapor phase. Thus, it appears that most osmium lost during copper refining would be emitted as a vapor. An unknown fraction of this compound, however, could be absorbed on the particulates in the stack gas. Removal of OsO_4 from stack gases by any control process other than chemical scrubbing is highly unlikely.

The osmium that might be entering the environment from this source cannot be accurately estimated. No data were found on the osmium content of crude ores. It has been estimated, however, that about 1 oz of platinum-group

metals is recovered per 6000 tons of ore (6). Bureau of Mines statistics show that about 258 million tons of copper ore were mined in 1970. Probably over 80% of this copper is mined as the sulfide ore.

Each major step in ore processing must be considered in attempting to determine where osmium losses might occur. The major steps in producing copper metal from low-grade sulfide ore are beneficiation, roasting, converting, and refining.

Flotation is commonly used to concentrate the ore after it has been crushed, ground, and classified. No information is available on how much of the platinum metals might be lost during this operation.

Roasting is conducted in a reducing or at least a nonoxidizing atmosphere to produce a copper matte, which consists of a mixture of Cu_2S and FeS. The composition of this matte may contain from 15 to 50% copper. Precious metals in the concentrate dissolve in this matte. Production of a high-grade matte can result in poor recovery of precious metals. Some osmium loss could occur during this operation, probably as a consequence of inadequate recovery rather than by oxidation and volatilization, even though the ore is subjected to temperatures of 1800°F in this operation.

Converting is the final stage in the smelting process and consists of passing a thin stream of air through the molten matte to oxidize the FeS to eliminate the sulfur as SO_2 and to form a ferrous slag and blister copper. The temperature of the molten matte is 1800°F. It is during this operation that the greatest osmium loss would occur. When precious metal concentrates are calcined, to eliminate S, Se, etc., it was found that more than 95% of the osmium is volatilized at 1700°F (8).

Although less osmium should be volatilized during the converting of copper matte to blister copper than during the calcining of precious metal concentrates, substantial losses likely occur during this operation. None of the gaseous effluent control devices presently in use would recover vaporized osmium tetroxide.

The final step in copper refining involves electro- or fire-refining of the blister copper. Substantial losses of osmium could occur during the latter process, which includes an oxidation

operation. After fire-refining, the metal may be cast into anodes suitable for electrolytic refining. It is the anode slimes remaining after electrolysis that are processed for platinum metals. Most blister copper in the U.S. is electrolytically refined.

The small amount of osmium recovered annually as a by-product of copper refining is only a fraction of that present in the original ore, probably less than 10%. Thus, 1000−3000 oz osmium is probably being lost to the environment each year from copper smelters.

Osmium consumed in manufacturing, generally as catalysts, is commonly recycled and reused many times. Unavoidable losses during production, however, account for a significant portion of the annual sales to the chemical manufacturing industry. All manufacturing organizations contacted indicated that they reprocess and reclaim osmium. Waste osmium lost by these users is commonly flushed down the drain, generally with no pretreatment to control toxicity. Because of the high organic content of most wastewater, it is probable that almost all of the osmium, particularly osmium tetroxide, is reduced either to osmium dioxide or to osmium metal soon after it reaches the wastewater stream.

The fate of osmium in wastewater is not known. The majority of osmium disposed of by pouring down the drain will be removed in the sludge. Soluble forms remaining in the water could be converted to osmium tetroxide during the chlorination operation and volatilized into the air. However, the majority of the soluble osmium should pass through the chlorination process unaffected. The small percentage present as osmium tetroxide will react rapidly and completely with residual organic matter in the receiving stream and be converted to osmium metal or to osmium dioxide and settle out in the sediment of the water course. The extremely low levels of osmium expected to be found in wastewater streams should pose no hazards to man or his environment.

The small amount of osmium metal disposed of as solid waste is resistant to chemical attack, and because of its wide dispersal into the environment should pose no health hazard. The only situation which could create a hazard consists of incineration of wastes containing os-

mium metal. Under incineration conditions, the osmium will be converted to volatile osmium tetroxide. However, the quantities which would normally be found in solid waste to be incinerated are probably too small to pose a hazard.

Health Hazards

Metallic osmium is considered inert (22). However, when heated in air or in a finely divided form at room temperature, it oxidizes to form osmium tetroxide. This water-soluble compound is volatile, highly irritant, and toxic. Natural and synthetic osmium-iridium alloys also give off osmium tetroxide during the gentle heating of annealing (23).

In absence of data to the contrary, it should be assumed that other soluble compounds of osmium, at least those in the higher valence state, are also toxic. Finely divided or spongy osmium metal is pyrophoric and should be handled with care. However, osmium dioxide, which is believed to be a product of the reduction reaction when osmium tetroxide reacts with organic materials, is considered to be inert. Following is a discussion of the acute and chronic effects of osmium tetroxide on animals and humans.

Vauquelin (24), Berzelius (25), Wöhler (26), Branell (27), and Bardieux (28) noted the corrosive action of osmium tetroxide on the respiratory tract and eyes. Subcutaneous or intramuscular injection of a 1% osmic acid solution did not cause serious effects, but small amounts injected into the lungs were immediately fatal (28).

One of the earliest references to a study of the toxicity of osmium was by Gmelin (29) in 1827. He reported that injection of 9−9.5 drams of "a fluid which held osmium in solution" (no concentration was reported) into the stomachs of a dog and a rabbit caused incessant vomiting in the dog and weakened the rabbit so that a second injection 4 days later was fatal. Tissues contacting the osmium tetroxide were blackened (the usual effect when osmium tetroxide is reduced by organic matter).

An extensive study of the effects of osmium tetroxide vapors was reported by Brunot in 1933 (23). He exposed rabbits for 30 min to osmic acid vapors in an air-tight glass box of 190-l. capacity equipped with a fan for circulation. Ampules containing 250, 500, and 1000 mg of osmic acid were placed on a watch glass on a hot plate in the chamber. Total vaporization occurred within 1−3 min. Since the osmium tetroxide was rapidly reduced by contact with the rabbits' skin, hair, mucous membranes, and excreta and by the glass walls, there is no way of knowing the vapor concentration in the air of the box.

Shortly after exposure began, the rabbits exhibited acute mucous membrane irritation and became semicomatose with a transient recovery after cessation of exposure. All of the rabbits developed pulmonary embarrassment. The animals exposed to 1000 mg lived an average of 30 hr and those exposed to 250 mg an average of 4 days. The lungs showed a purulent bronchopheumonia and were swollen with a blood-stained fluid. The epithelial lining of the bronchi and bronchioli was colored dark red, and many bronchi were ulcerated and pus-filled. The trachea was necrotic and plugged with leucocytes. The kidneys showed moderately cloudy swelling and granulation of the tubular epithelium.

Both exposure to the vapor and instillation of a 1% aqueous solution of osmium tetroxide solution into the conjunctival sac colored the latter, as well as the sclera and cornea brown and caused edema, a purulent discharge, and a residual corneal opacity and pannus.

Chronic exposure of guinea pigs to vapor from ampuls containing 50 mg osmium tetroxide for 8 hr daily produced death in about 60 days (30). The guinea pigs suffered from a chronic anemia with an initial hyperactivity of the bone marrow. The final decrease in the formed elements of the blood suggested that osmium is toxic to the bone marrow.

Anatamopathological changes occurring in the organs of rabbits acutely and chronically poisoned with osmium tetroxide vapors were reported by Masturzo in 1950 (31). Rabbits acutely poisoned by vapors from 125 mg osmium tetroxide in aqueous solution in a chamber 0.60 × 0.40 × 0.50 (units not given) for 24−48 hr showed degenerative and congestive changes, particularly of the lungs, but also of the liver, spleen, kidney, and adrenals. The heart, thyroid, and testes showed only slight changes. The rabbits chronically poisoned for 8

hr daily with vapors from an aqueous solution containing 50 mg osmium tetroxide and sacrificed after exposures of 45−60 days showed marked sclerosis and collapse of lung tissue, bronchial compression, congestion and degeneration of the liver, sclerosis of the spleen, and fatty degeneration of the kidney and adrenals.

Osmium tetroxide (1 ppm) ingested together with 0.5 ppm ammonium molybdate and 1 ppm cobalt sulfate was reported to have delayed death from the necrotic liver degeneration of rats that had been fed diets containing yeasts as the sole protein source. Osmium given alone, however, protected only some of the animals (32). Later studies by Schwarz, Roginski, and Foltz (33) did not confirm these results.

The acute effects of osmium tetroxide vapors in humans are similar to those in animals: there is chiefly eye and respiratory tract damage.

Exposure to an unknown ambient air concentration of osmium tetroxide vapor during extraction of osmium from platinum residues imparted near blindness to one researcher for 24 hr (34). The resulting conjunctivitis persisted for weeks. Cases of permanent blindness have also been reported (23).

Refinery workers, exposed to osmium tetroxide concentrations of 133-640 $\mu g/m^3$ in the fine spray produced in dissolving osmiridium ores in aqua regia, experienced a gritty feeling in the eyes with pain and lacrimation (35). The workers saw large haloes around lights and were unable to read or see motion pictures during the height of the symptoms, which generally subsided within 24 hr.

Eye irritation in precious-metals workers and among histologists, who use 1−2% osmic acid solutions as a stain, is commonly accompanied by frontal or orbital headache (35).

Asthma and dyspnea were noted by Deville and Debray (34) while they were extracting osmium from osmiridium; by Brunot (23), after opening four 250-mg ampules of osmium tetroxide; and by McLaughlin (35) in one of seven workers studied who were engaged in refining osmiridium.

One authenticated death following accidental inhalation of osmium tetroxide vapor was attributed to bronchial pneumonia (23,36). The conditions of the accident and the vapor concentration, however, were not reported. The postmortem lesions revealed capillary bronchitis, bronchial pneumonia with a tendency to suppuration and gangrene, and fatty degeneration of the renal tubule epithelium.

Obviously, workers dealing with metallic osmium should be protected from the hazards of osmium tetroxide vapor by adequate ventilation. Although Flury and Zernick report that the highest concentration that can be tolerated for 6 hr without harmful effects is 0.001 mg/m^3, the American Conference of Governmental Industrial Hygienists set 0.002 mg/m^3 as the threshold-limit value for osmium tetroxide in 1971 (37). Laboratory workers using osmium tetroxide tissue-straining solutions should be alerted to the possible dangers, even at these low concentrations. -

Dreisbach estimated the fatal dose of orally ingested osmic acid as 1 g, with an acidlike corrosive effect ranked as 4 on a scale of 1 to 4. The rank of 4 denotes complete destruction of skin or mucous membrane (38).

Few data are available that provide information on possible chronic human effects of nonacute exposure resulting from environmental contamination by osmium. Workers continually exposed to osmium tetroxide vapors (refiners and histologists) and rheumatoid arthritis patients who have received intra-articular osmic acid injections have shown no apparent permanent damage from exposure to low levels of osmium.

Osmium has been used with apparently little success, but no ill effects in the treatment of conditions including epithelioma, peripheral neuritis, syphilis, and tuberculosis (35,39).

Presumably, 1% osmic acid solutions used for chemical synovectomy of arthritic joints are without harmful systemic effects in nonallergic patients. Most of the injected osmium is excreted in the urine with none accumulating in the contralateral knee, the regional lymph nodes, the liver, or the heart (40). The method is reportedly used routinely in Finland for chemical synovectomy of afflicted knee joints of both adults and juveniles. Osmic acid injections into the knees of patients 2−15 years of age did not cause disturbances of growth, cartilage, or bone, as might be expected if the growing joints had been damaged (41). Verhaeghe et al. in

France have recommended the use of intraarticular injections of 1% osmic acid into the hip, the ankle, the wrist, the elbow, and the shoulder, as well as the knee (42).

According to animal experiments, osmic acid, used in intra-articular therapy of rheumatoid arthritis patients for chemical synovectomy, mechanically coagulates the endothelial layer of the synovial membrane (40), which disappears within some days (43). Immediately after the initial tissue injury, enzyme activities are decreased and blood flow is arrested (43,45). Ultimately, undamaged underlying tissues regenerate a new thickened synovial membrane. Osmium pigment remains in the deeper synovial-tissue layer for up to 9 months after injection (18). In human patients, the osmium remaining in the synovial membrane for long periods (> 30% of that injected) is partly phagocytized in macrophages or giant cells, part remains in the cytosomes of the synovial-membrane cells, and part is fixed in fat cells (46).

Skin irritations and (or) allergic reactions to osmic acid solutions are seldom reported. A few cases of dermatitis, eczema, or urticaria have been attributed to topical contact with osmic acid solutions while extracting osmium from osmiridium (34,39) or taking fingerprints (47) or to intra-articular injections (41,48). One arthritic patient, who had a history of drug allergy, experienced an acute immune response on receiving her second osmic acid injection 4 yr after the first. After the acute phase, the kidney and liver damage that occurred disappeared within a week (49).

Conclusions

Based on this survey, we have concluded that the toxicity of osmium tetroxide, although well recognized, poses no serious health hazard when this compound is handled by recommended procedures and with adequate caution.

No large localized loss of osmium sufficient to create an obvious environmental hazard has been identified.

Copper refineries are a potential source of osmium contamination. However, there are insufficient data to assess the magnitude of contamination from this source.

There are insufficient data to define the chronic toxicity of osmium compounds.

Procedures should be developed for handling and disposing of osmium compounds, particularly in research laboratories.

Acknowledgments

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